Synthesis of Highly Ordered TiO$_2$ Nanotube in Malonic Acid Solution by Anodization

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We synthesized TiO$_2$ nanotube array by anodizing in a solution of malonic acid (HOOCCH$_2$COOH) and NH$_4$F, and analyzed the morphology of the nanotube using scanning electron microscopy (SEM). The morphology of TiO$_2$ nanotube was largely affected by anodizing time, anodizing voltage, and malonic acid concentration. With increasing the anodizing voltage from 5 V to 20 V, the diameter of TiO$_2$ nanotube was increased from about 20 nm to 110 nm and its length from about 10 nm to 700 nm. In addition, the length of TiO$_2$ nanotube was increased with increasing anodizing time up to 6 h at 20 V. We obtained the longest and the most highly ordered nanotube structure when anodizing Ti in a solution of 0.5 wt% NH$_4$F and 1 M malonic acid solution at 20 V for 6 h.

Keywords: TiO$_2$ Nanotube, Malonic Acid, Anodizing, Highly Ordered Structure.

1. INTRODUCTION

Over the past several years, TiO$_2$ nanotube has been extensively studied because it has a variety of functional properties for the applications in gas sensing, self-cleaning, solar cell, photo-catalysis, and electroplating. Many researchers have synthesized TiO$_2$ nanotube in aqueous solution containing HF, since Zwilling et al. synthesized TiO$_2$ nanotube in the H$_2$O/HF solution for the first time. In solutions containing aggressive F$^-$ ion at high applied voltage, pores can be initially formed on the entire surface of Ti by pitting corrosion. In particular, the TiO$_2$ at the bottom of pores combines with F$^-$ ion and dissolves into electrolyte as a form of soluble TiF$_2$. This chemical dissolution process develops typical nanotube structure and controls the length of nanotube. In addition, Macak et al. found that it is effective to add some buffer species such as SO$_2$$_4$ and PO$_3$$_4$ into anodizing solutions to obtain TiO$_2$ nanotube structure with high aspect ratio. These buffer species suppress the sudden increase in solution pH at the mouth of nanotube, and maintain the pH gradient from the mouth to the bottom of the tube that is necessary for the growth of nanotube.

Recently, some researchers reported that some organic species could be effectively used as a buffer species for the synthesis of TiO$_2$ nanotube in non-aqueous solutions. However, thus far, few studies have reported the effect of organic species as a buffer species on the formation of TiO$_2$ nanotube in the aqueous solution.

In this study, we synthesized TiO$_2$ nanotube in an aqueous solution of malonic acid (HOOCCH$_2$COOH) as a new buffer ion source and NH$_4$F as a F$^-$ ion source for the first time. Furthermore, we investigated the effects of concentration of malonic acid, anodization voltage and anodization time on the structure of TiO$_2$ nanotube.

2. EXPERIMENTAL DETAILS

A commercially pure Ti foil 0.05 mm thick was degreased with acetone followed by rinsing with deionized water and drying. For anodizing, we used Ti sample with the exposure area of 1 cm$^2$ as a working electrode and Pt plate as a counter electrode. Anodizing was performed in solutions of 0.5 wt% NH$_4$F and x M malonic acid ($x = 0$∼$2$) by varying anodizing time from 1 min to 6 h. Voltages from 5 V to 20 V were applied on the specimen using DC power supply, and the corresponding current was recorded using an attached digital multimeter. All anodizing experiments were conducted at an ambient temperature (22 ± 2 °C). The surface and cross-sectional morphologies of the TiO$_2$ nanotube were analyzed using scanning electron microscope (SEM).
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1 µm

Fig. 1. Surface and cross-sectional morphologies of TiO$_2$ nanotubes obtained from anodizing Ti for 1 h at 20 V in solutions of 0.5 wt% NH$_4$F and $x$ M malonic acid; (a) 0 M, (b) 0.1 M, (c) 1 M and (d) 2 M.

3. RESULTS AND DISCUSSION

3.1. Effect of Concentration of Malonic Acid

Figure 1 shows the effect of concentration of malonic acid on the surface and cross-sectional morphologies of Ti anodized in solutions of 0.5 wt% NH$_4$F and $x$ M malonic acid ($x = 0$–2) at 20 V for 1 h. Non-uniform formation of nanotubes was observed on the sample anodized in the solution without malonic acid. In contrast, TiO$_2$ nanotubes were formed uniformly on the samples anodized in the solutions containing malonic acid. The uniformity of nanotube array is attributed to the buffer effect of malonic acid ion. Malonic acid ion as a buffer species contributes to suppress the sudden increase in solution pH at the tube mouth and maintains the pH gradient from mouth to bottom of tube for the growth of nanotubes. Furthermore, the concentration of malonic acid affected the length of TiO$_2$ nanotube as well as the uniformity of the nanotube array. The length of nanotube increased with increasing the concentration of malonic acid up to 1 M. However, the length of nanotube decreased slightly in 2 M solution. This phenomenon indicates that there is an optimum concentration of malonic acid for the growth of nanotube. The main role of malonic acid is to maintain the pH gradient in the tube by suppressing the increase in pH at tube mouth. For the stable longitudinal growth of nanotube, chemical dissolution should be concentrated only at the tube bottom with low solution pH. However, excessive addition of malonic acid can induce the overall increase in solution pH of entire tube region including tube bottom.

Figure 2 shows the effect of malonic acid concentration on the current variation during anodizing. The stabilized mean current density measured in the solution without malonic acid was smaller than that with malonic acid. In addition, the current for the sample anodized in the solution without malonic acid fluctuated much less than that with malonic acid. For the samples anodized in the solution with malonic acid, current density was decreased by the formation of barrier film in the early stage of anodizing and then stabilized. Furthermore, the period of time required to reach steady state was increased with increasing malonic acid concentration from 0.1 M to 2 M.

Fig. 2. Current transient curves for Ti anodized for 1 h at 20 V in solutions of 0.5 wt% NH$_4$F and $x$ M malonic acid; (a) 0 M, (b) 0.1 M, (c) 1 M and (d) 2 M.
3.2. Effect of Anodizing Time

Figure 3 shows the effect of anodizing time from 10 min to 6 h on the cross-sectional morphologies of nanotubes obtained from anodizing in a solution of 0.5 wt% NH₄F and 1 M malonic acid at 20 V. The uniform surface covered with TiO₂ nanotubes was obtained from the samples anodized for 30 min. The average diameter of TiO₂ nanotubes on the sample anodized for 30 min was approximately 110 nm. On the whole, the length of TiO₂ nanotubes increased with increasing anodizing time. However, the length and diameter of TiO₂ nanotubes reached steady values after 6 h. This phenomenon indicates that it is not easy for the nanotube to grow any more once

Fig. 3. Cross-sectional morphologies of TiO₂ nanotubes obtained from anodizing Ti at 20 V in a solution of 0.5 wt% NH₄F and 1 M malonic acid for (a) 10 min, (b) 30 min, (c) 1 h and (d) 6 h.

Fig. 4. Surface and cross-sectional morphologies of TiO₂ nanotubes obtained from anodizing Ti for 1 h in a solution of 0.5 wt% NH₄F and 1 M malonic acid at (a) 5 V, (b) 10 V, (c) 15 V and (d) 20 V.
3.3. Effect of Anodizing Voltage

Figure 4 shows the effect of anodizing voltage (5 V, 10 V, 15 V and 20 V) on the surface and cross-sectional morphologies of TiO$_2$ nanotubes obtained from anodizing in a solution of 0.5 wt% NH$_4$F and 1 M malonic acid for 1 h. With increasing anodizing voltage from 5 V to 20 V, the diameter and length of TiO$_2$ nanotube varied from about 20 nm to 110 nm and from 10 nm to 700 nm, respectively, as shown in Figure 4. It is noticeable that the diameter and length of nanotube can be easily controlled by varying anodizing voltage. The range of nanotube diameter in this study is similar to that reported in the previous work using a solution of H$_3$PO$_4$ and HF for anodizing.\footnote{J. M. Macak, M. Lamac, J. Krysa, and P. Schmuki, Small 3, 300 (2007).}

Figure 5 shows the current transient curves corresponding to the samples anodized at various anodizing voltage. The mean current densities of the samples were similar to each other as about 2 mA cm$^{-2}$. However, the current fluctuation was significantly reduced with increasing the anodizing voltage from 5 V to 20 V. The decrease in current fluctuation indicates the suppression of pH burst, i.e., the sudden decrease in pH at the pore entrance.\footnote{J. M. Macak, H. Tsuchiya, and P. Schmuki, Angew. Chem. Int. Ed. 44, 2100 (2005).}

The broad controllable range of nanotube diameter obtained from this study is expected to ensure a variety of its applications where the control of tube diameter is important. For example, in Cu electrodeposition, the nucleation density of Cu on Ti cathode was reported to be highly sensitive to pore density and diameter.\footnote{M. Paulose, K. Shankar, S. Yoriya, H. E. Prakasham, O. K. Varghese, G. K. Moz, T. A. Latempa, A. Fitzgerald, and C. A. Grimes, J. Phys. Chem. B 110, 16179 (2006).}

4. CONCLUSION

The highly ordered TiO$_2$ nanotubes were synthesized in malonic acid solution by anodizing method. The morphology of TiO$_2$ nanotube was largely affected by anodizing time, anodizing voltage, and malonic acid concentration. With increasing the anodizing voltage from 5 V to 20 V, the diameter of TiO$_2$ nanotube was increased from about 20 nm to 110 nm and its length from about 10 nm to 700 nm. In addition, the length of TiO$_2$ nanotube was increased with increasing anodizing time up to 6 h at 20 V. We obtained the longest and the most highly ordered nanotube structure when anodizing Ti in a solution of 0.5 wt% NH$_4$F and 1 M malonic acid at 20 V for 1 h.

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